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SHALLOW IMPURITIES IN SEMICONDUCTOR QUANTUM WELLS

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ABSTRACT

Theoretical calculations on the binding energies of shallow impurities (donor and acceptors) in semiconductor quantum wells are reviewed.

1. INTRODUCTION

Shallow impurities play important roles in determining the electronic and optical properties of semiconductors quantum wells and superlattices. Bastard[1] first attacked this problem by considering a hydrogenic impurity in a quantum well with infinite barrier height. The model predicts that the binding energy of an impurity placed at the center (or edge) of the well decreases from $4 \, R_o$ monotonically to $1 \, R_o$ (or $0.25 \, R_o$) for well width from zero (two-dimensional limit) to infinity (three-dimensional limit), where $R_o$, the effective rydberg is the binding energy of a three-dimensional hydrogenic impurity. Mailhoit et al.[2] and Green and Bajaj[3] independently calculated the energies of the ground state and a few excited states of a hydrogenic impurity in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum well, using variational method. For donors in realistic quantum wells (with finite barrier height), the impurity binding energy as a function of the well width is found to have a maximum at a critical width around 20-50 Å, instead of increasing monotonically from the bulk value to the two-dimensional limit of $4 \, R_o$. This is because the impurity wavefunction begins to leak out the well material ($\text{GaAs}$) into the barrier material ($\text{Al}_x\text{Ga}_{1-x}\text{As}$) as the well width becomes smaller than the critical width, and the impurity binding energy eventually approaches the bulk value of the barrier material ($\text{Al}_x\text{Ga}_{1-x}\text{As}$) (which is smaller than $4 \, R_o$) as the well width goes to zero.

Chaudhuri[4] examined the case where a hydrogenic impurity is placed at the center of a $\text{Al}_x\text{Ga}_{1-x}\text{As}$ multiple quantum well. He found that the impurity binding energy as a function of the well width (= barrier width) exhibits a double-peak structure, with the two peaks occuring at well widths of approximately 10Å and 100Å.

Various experimental measurements of the electronic levels of donors in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum wells have recently been reported. These measurements include photoluminescence[5], Raman scattering[6] and far-infrared magneto-spectroscopy[7]. The photoluminescence detects the free heavy-hole to donor transition and by comparing it with the heavy-hole exciton transition, one can deduce the difference between the donor binding energy and the exciton binding energy. Shanabrook and Comas[5] has found that the donor binding energy is consistently lower than the exciton binding energy by 1-2 meV for quantum wells with widths between 80-450 Å. Raman scattering[6] measures the energy separation between the ground state (1s) and the first even-parity excited state (2s). The measurements are in good agreement with the theoretical predictions of Mailhiot et al.[2].
Far-infrared magnetospectroscopy [7] measures the energy separation between the ground state and the first odd-parity excited state (2p_e). This measurement is more sensitive and less ambiguous than the previous measurements. The results are found in good agreement with the theoretical predictions by Greene and Bajaj [8].

Shallow acceptors in quantum wells were first studied experimentally by Miller et al. [9]. They observed the photoluminescence due to recombination of n = 1 free electrons with neutral acceptors. By measuring the energy separation between this peak and the heavy-hole exciton recombination peak, one can determine the acceptor binding energy to within 2 meV (the uncertainty of the theoretical exciton binding energy). Determination of the acceptor binding energy by photoluminescence is more reliable than that of the donor binding energy, because the free electron to acceptor transition is well separated from other transitions such as the bound exciton recombinations which often obscure the free hole to donor transition. Furthermore the relatively large binding energies of acceptors make the uncertainty in determining the free exciton binding energy a less serious problem. Theoretical calculations of the energy spectra of acceptors in Al_x Ga_{1-x} As-GaAs quantum wells were recently undertaken by Masseink et al. [10]. These calculations take into account the coupling of the top four valence bands of both the well and barrier materials. The theoretical results are found in good agreement with the available experimental data, when the valence band discontinuity between GaAs and Al_x Ga_{1-x} As is taken to be 35% of the energy gap difference. For quantum wells of widths comparable to the acceptor radius (about 30 Å), the acceptor binding energy is quite sensitive to the choice of the valence band discontinuity. Thus, for new quantum well structures (such as GaAs-GaInAs, GaSb-AlSb, etc.), comparing the measured acceptor binding energy with the theoretical prediction can provide a clue to their valence band discontinuity.

II. DONORS IN QUANTUM WELLS

Within the effective mass approximation, the Hamiltonian for a hydrogenic donor in the quantum well is given by

$$\hat{H}_D(\vec{r}) = \frac{-\hbar^2}{2m^*_w(z)} \nabla^2 + V(z) - v(\vec{r}),$$

where $m^*_w(z) = m^*_w$ (effective mass of the well material) for z inside the well and $m^*_b$ (effective mass of the barrier material) for z outside. $V(z)$ is the quantum well potential, which is a constant $-V_0$ for z inside the well and zero outside. $v(\vec{r})$ is the Coulomb potential describing the interaction between an electron and the donor impurity, $v(\vec{r}) = -\frac{e^2}{\varepsilon(z)\varepsilon_0 r}$, where $\varepsilon(z)$ is the static dielectric constant for the well or barrier material, depending on where z is. Because the dielectric constants for the well and barrier materials are different, image charges induced by the donor impurity should in principle be included. Such image charges have been taken into account in the calculations of Mailhiot et al. [2]. Here, for simplicity, we shall ignore the effect of image charges.

The Rayleigh-Ritz variational method is used to obtain the energy spectra of bound states associated with $\hat{H}_D$. The eigenstates of $\hat{H}_D$ (i.e. donor state envelope functions) are expanded in terms of linear combinations of a set of basis functions $\{\phi_n(\vec{r})\}$, i.e., $F(\vec{r}) = \sum_n C_n \phi_n(\vec{r})$. The expansion coefficients $C_n$ and the eigenvalue
5 can be found by solving the secular equation

\[ \sum_{n} \langle \beta_{n}|\hat{H}_{D}-E|\beta_{n}\rangle C_{n} = 0. \]  

(2)

Since the effective masses for the well and barrier materials are different, special boundary conditions for the basis functions and therefore \( \psi(\vec{r}) \) must be satisfied such that the current \( J \sim \frac{\hbar}{m_{\text{eff}}} \psi^{*} \frac{\partial}{\partial z} \psi \) is continuous. Failure of choosing basis functions which satisfy the boundary conditions would result in an unphysical non-hermitian Hamiltonian matrix, \( \langle \beta_{n}|\hat{H}_{D}|\beta_{n}\rangle \). For even-parity states (s-like), Mailhiot et al. [2] have used Gaussian-type basis functions of the form:

\[ \beta^{(1)}(\vec{r}) = a(z) \exp \left(-\zeta(z)(x^{2}+y^{2}+z^{2})\right), \]  

(3)

where

\[ \zeta(z) = \begin{cases} \sigma_{W} & \text{for } |z| < W/2 \\ \sigma_{B} & \text{for } |z| > W/2 \end{cases} \]  

(4)

and

\[ a(z) = \begin{cases} a_{W} \exp \left[(\sigma-1) \sigma_{W}(W/2)^{2}\right] & \text{for } |z| < W/2. \end{cases} \]  

(5)

The special relations between Gaussian exponents and prefactors inside and outside the well ensure the continuity of the wave function \( \psi(\vec{r}) \) and \( \frac{1}{m(z)} \frac{\partial}{\partial z} \psi(\vec{r}) \). \( \lambda \) is a variational parameter, which is adjusted to minimize the energy. Green and Bajaj [10] used a basis set which is capable of describing the donor states accurately for both narrow and wide wells. However, they considered the problem in which both the well and barrier materials have the same effective mass. Therefore, in the zero-width limit, their results are identical to those for bulk GaAs instead of Al\(_{x}\)Ga\(_{1-x}\)As. It is possible to improve the calculations of Mailhiot et al. [2] and that of Green and Bajaj [8] by choosing a basis set containing two types of states. Type 1 is identical to the basis set used by Mailhiot et al., i.e. \( \beta^{(1)}(\vec{r}) \) as given in (3). Type 2 has the form

\[ \beta^{(2)}(\vec{r}) = f_{n}(z) \exp \left[-\alpha(x^{2}+y^{2})\right] \]  

where \( f_{n}(z) \) is the nth eigenstate (\( n \) is the principal quantum number) of the quantum well Hamiltonian,

\[ H(0)(z) \equiv \left[-\frac{\hbar^{2}}{2m(z)} \frac{\partial^{2}}{\partial z^{2}} + V(z)\right]. \]  

For calculating the ground state, use \( n = 1 \). For ease in computation, \( f_{n}(z) \) is again written as a linear combination of Gaussian-type orbitals with proper boundary conditions, i.e.

\[ f_{n}(z) = \sum_{k} C_{k} a_{k}(z) \exp \left[-\zeta_{k}(z) z^{2}\right] \]  

where \( C_{k}(z) \) and \( a_{k}(z) \) take the forms described in (4) and (5). The coefficients \( C_{k} \) are obtained by solving the Schrödinger equation \( H(0)(z) f_{n}(z) = E_{n}(0) f_{n}(z) \).

Solving (2) within the basis set described above gives the eigenvalues of the Hamiltonian. With sufficiently large basis set (about 9 Gaussian-type orbitals for each type) and varying the parameter \( \lambda \) to minimize the energy,
accurate energy spectra for the low-lying states can be obtained. Fig. 1 shows the ground state energy of the center-doped donor impurity in $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ quantum well as a function of well width measured with respect to the bottom of the first conduction subband of the quantum well $(E_1^{(0)})$. The conduction band offset is chosen to be 65% of the energy gap difference between the well and barrier materials[11]; whereas in previous calculations[2] a value of 85% was used. As a consequence, the results for $x = 0.4$ obtained here correspond approximately to the results for $x = 0.3$ obtained in previous calculations. In this figure, the dashed curves are obtained with type 2 basis only and the solid curves are obtained with combined basis set. For well width between 20Å and 200Å, the difference in binding energy between the two sets of curves is less than 5%.

![Fig. 1. Binding energies of donors at the center of $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ quantum wells as functions of well width.](image)

III. ACCEPTORS IN QUANTUM WELLS

In the presence of quantum well potential and Couloum interaction with an ideal acceptor impurity, we write the eigenstates of the system as linear combinations of bulk valence band Bloch states, viz.

$$\Psi(r) = \sum \tilde{f}_v(k) e^{ik\cdot r} |v,\hat{k}\rangle$$

(6)

where $|v,\hat{k}\rangle$ are cell-periodic functions, correct to first order in the $\hat{k} \cdot \hat{p}$. 
perturbation[12]; \( v = (J,M) \) with \( J = 3/2, 1/2 \) and \( M = -J, \ldots, J \). \( \tilde{F}_v (\vec{k}) \) are Fourier transforms of acceptor envelope functions, \( F_v (\vec{r}) \). Within the effective-mass approximation, it can be shown that \( F_v (\vec{r}) \) satisfy the equation

$$
\sum_{v'} [ -H_{vv'}^{(0)} (-i\nabla) + [V(z) + v(\vec{r})] \delta_{vv'} ] |F_v (\vec{r}) = E |F_v (\vec{r}),
$$

(7)

where \( H_{vv'}^{(0)} (-i\nabla) \) are matrix elements of the Luttinger-Kohn Hamiltonian[13] \( H_{vv'}^{(0)} (\vec{k}) \) with \( \vec{k} \) replaced by the operator \(-i\nabla\). Note that the Luttinger parameters \( \gamma_1, \gamma_2 \) and \( \gamma_3 \) take on two different values for \( z \) inside and outside the well. Three parameters are listed in Table II of Ref. 14 for all materials of interest here. \( V(z) \) is the quantum well potential for holes and \( v(\vec{r}) \) is the Coulomb potential for the ideal acceptor.

For semiconductors with spin-orbit splitting (\( \Lambda \)) much larger than the acceptor binding energy, the split-off states \( (J = 1/2) \) may be ignored. This is true for \( Al_x Ga_{1-x} As - GaAs \) and \( GaAs - Ga_{1-x} In_x As \) systems. For \( Si - Si_{1-x} Ge_x \) systems, which are attracting a great deal of interest recently, the split-off states must be included. In the present paper, we shall only consider systems with large spin-orbit interactions. We shall only use the upper-left \( 4\times4 \) block of the matrix \( H_{vv'}^{(0)} (\vec{k}) \).

To solve (7) for the acceptor spectra in quantum wells, we expand the envelope function \( F_v (\vec{r}) \) in terms of linear combinations of a set of basis functions \( \{ \beta_n^v (\vec{r}) \} \), i.e., \( F_v (\vec{r}) = \sum_n C_n^v \beta_n^v (\vec{r}) \). The expansion coefficients and the eigenvalue \( E \) can be found by solving the secular equation

$$
\sum_{v',n'} <\beta_{n'}^{v'} | H^{(A)}_{vv'} - E |\beta_n^v > C_{n'}^{v'} = 0
$$

(8)

where \( H^{(A)}_{vv'} = -H_{vv'}^{(0)} (-i\nabla) + [V(z) + v(\vec{r})] \delta_{vv'} \).

The forms of the basis functions are chosen such that the symmetry properties of the Hamiltonian \( H^{(A)} \) are fully exploited. In general, all basis functions \( \beta_n^v (\vec{r}) \) can be written as a radial function \( f_n (r) \) multiplied by a spherical harmonics. Because the quantum well potential \( V(z) \) has a preferential direction, it is advantageous to replace the radial function \( f_n (r) \) by an ellipsoidal function \( f_n (r') \), where \( r' \equiv \sqrt{x^2 + y^2 + \lambda^2 z^2} \) with \( \lambda \) to be adjusted to produce fastest convergence. If the best value of \( \lambda \) is chosen, then we only need a small number of spherical harmonics to produce good results. We shall only include spherical harmonics of \( \ell = 0, 1, \) and 2 in our calculation.

For center-doped acceptors in quantum wells, the effective-mass Hamiltonian has a \( D_{2d} \) symmetry and the double group irreducible representations are \( \Gamma^+ \) and \( \Gamma^- \) (both doubly degenerate)[15], where the superscript +(-) denotes parity. Here parity is a good quantum number, so \( \ell = 1 \) states are decoupled.
from \( I = 0 \) and 2 states. For the \( \Gamma_6^+ \) states, which are predominently heavy-hole like \((\nu = \pm 3/2)\), only six types of basis functions (one s-like and five d-like) need to be considered. These are

\[
\begin{align*}
\beta^v_1(\Gamma_6^+; \mathbf{r}) &= f_s(\mathbf{r'}) \delta_{\nu, 3/2} \\
\beta^v_2(\Gamma_6^+; \mathbf{r}) &= \left[ x^2 - \frac{1}{2} (y^2 + z^2) \right] f_s(\mathbf{r'}) \delta_{\nu, 3/2} \\
\beta^v_3(\Gamma_6^+; \mathbf{r}) &= \frac{\sqrt{3}}{2} (x^2 - y^2) f_s(\mathbf{r'}) \delta_{\nu, -1/2} \\
\beta^v_4(\Gamma_6^+; \mathbf{r}) &= \frac{i}{\sqrt{2}} (yz - ixz) f_s(\mathbf{r'}) \delta_{\nu, 1/2} \\
\beta^v_5(\Gamma_6^+; \mathbf{r}) &= 1xy f_s(\mathbf{r'}) \delta_{\nu, -1/2} \\
\beta^v_6(\Gamma_6^+; \mathbf{r}) &= \frac{i}{\sqrt{2}} (yz + ixz) f_s(\mathbf{r'}) \delta_{\nu, -3/2},
\end{align*}
\] (9)

where \( f_s(\mathbf{r'}) \) is an illipsoidal function, which we choose to have the Gaussian form,

\[
f_s(\mathbf{r}) = e^{-a(x^2 + y^2 + \lambda^2 z^2)}.
\] (10)

Note that \( \beta^v_6(\Gamma_6^+) \) does not couple directly to \( \beta^v_1(\Gamma_6^+) \) and \( \beta^v_2(\Gamma_6^+) \) [dominant terms in the ground and first excited states]. This type of basis function is ignored in our calculation. Similarly for the \( \Gamma_7^+ \) states (predominently light-hole like, \( \nu = \pm 1/2)\), only five types of basis functions (denoted \( \beta^v_n(\Gamma_7^+; \mathbf{r}) \); \( n = 1, \ldots, 5 \)) are used. They are simply related to the \( \Gamma_6^+ \) basis states by exchanging the indices: \( \pm 3/2 \leftrightarrow \pm 1/2 \).

The basis functions defined in (9) and (10) do not satisfy the boundary conditions appropriately. The calculation becomes rather cumbersome, if we use the same method as for the donor case to generate basis functions which satisfy the boundary conditions. The simplest method to circumvent this difficulty is to perform the calculation twice, once using the Luttinger parameters and dielectric constant appropriate for the well material and the other using parameters appropriate for the barrier material. The two sets of results are then averaged according to the probabilities of finding the hole inside and outside the quantum well[10].

Fig. 2 shows binding energies of the lowest \( \Gamma_6 \) and \( \Gamma_7 \) states for acceptors at the center of \( \text{Al}_{x}\text{Ga}_{1-x}\text{As-GaAs} \) quantum wells calculated by Masselink et al.[10] as functions of the well width for \( x = 0.1 \) and 0.3. The \( \Gamma_6 \) and \( \Gamma_7 \) acceptor binding energies are measured with respect to the top of
the first heavy-hole and light-hole subbands, respectively.

Effects of chemical shifts of various dopants on the acceptor binding energy in $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ quantum wells are also studied. The central-cell potential is modeled by the short-range potential $V_c = U_0 e^{-\left(\frac{r}{\tau_0}\right)^2}$, where $\tau_0 = 1$ Å and $U_0$ is adjusted to reproduce the acceptor binding energy in bulk GaAs measured experimentally. It is assumed that $U_0$ remains unchanged in the quantum well. Fig. 3 shows the $\Gamma_6$ ground state energies of center doped beryllium and carbon acceptors as functions of GaAs well width for $x = 0.3$. The parameter $U_0$ used is $-5.55$ eV for beryllium and $8.00$ eV for carbon. The experimental data for beryllium (open squares) [from Ref. 10] and carbon (open circles) [from Ref. 9] are also shown for comparison. Very good agreement between theory and experiment is found.

Fig. 2  Binding energies of lowest $\Gamma_6$ and $\Gamma_7$ states for ideal acceptors at the center of $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ quantum wells as functions of well width.

Fig. 3  Binding energies of beryllium and carbon acceptors at the center of $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ quantum wells as functions of well width, open squares: data for beryllium from Ref. 10, open circles: data for carbon from Ref. 9.
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